

Evidence for a capacitor network near the metal insulator transition in VO₂ thin films probed by in-plane impedance spectroscopy

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Impedance spectroscopy measurements were performed in high quality Vanadium dioxide (VO₂) thin films. This technique allows us investigate the resistive and capacitive contribution to the dielectric response near the metal-insulator transition (MIT). A non ideal RC behavior was found in our films from room temperature up to 334 K. A decrease of the total capacitance was found in this region, possibly due to interface effects. Above the MIT, the system behaves like a metal as expected, and a modified equivalent circuit is necessary to describe the impedance data adequately. Around the MIT, an increase of the total capacitance is observed.

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VO₂ exhibits a sharp first-order metal-insulator transition (MIT) and structural-phase transition (SPT) from a high temperature metallic rutile phase to a low temperature insulating monoclinic phase¹. VO₂ also shows phase separation during the transition², which leads to percolation and avalanches³. Potential applications range from bolometers⁴ to smart windows⁵. From the electronic point of view, the possibility to induce the MIT with an electric field⁶, opens a window in resistive non-volatile random access memory (ReRAM) using VO₂ as a switching element⁷. For applications in electronic devices the response of the MIT in VO₂ to an AC electrical field is crucial. Impedance Spectroscopy (IS) enables the many contributions to the dielectric and resistive properties of electroceramic materials to be deconvoluted and characterized individually. The charge transport mechanism consists of several contributions such as sample-electrode interface and bulk resistance/capacitance. IS is shown to be a powerful tool to model such behavior. Recently, impedance spectroscopy (IS) has been used to investigate the MIT in ZnO nano-powders^{8,9}, the resistive switching in NiO and TiO₂ thin films^{10,11}, magnetoimpedance in MgO tunnel barriers¹², surface passivation in silicon¹³ and BiMnO₃ thin films¹⁴. In each cases, IS gives relevant information about AC conduction.

Recently, AC voltage-current measurements were performed by Lee et. al. in two-terminal VO₂-based devices, where MIT oscillations were found⁶. They attributed these to be the result of the presence of non-VO₂ phases, which results in a large capacitive component around 156 pF. A detailed study of the electrical response in a full-range frequency in VO₂ thin films has not been done. In this letter a series of Impedance Spectroscopy (IS) measurements are described. These were performed in order to study the dielectric response of VO₂ thin films as a function of frequency of an AC electrical field across the

MIT and deconvoluted several contributions.

Highly (00 ℓ)-oriented vanadium di-oxide thin films were prepared by reactive RF magnetron sputtering from a 99.8% vanadium target (1.5" diameter) on r-cut (10 $\bar{1}2$) sapphire substrates. The films were deposited in a high-vacuum deposition system with a base pressure of 5×10^{-8} Torr¹⁵.

In-plane IS measurements were performed using an HP 4194A Impedance analyzer in the frequency range of 100

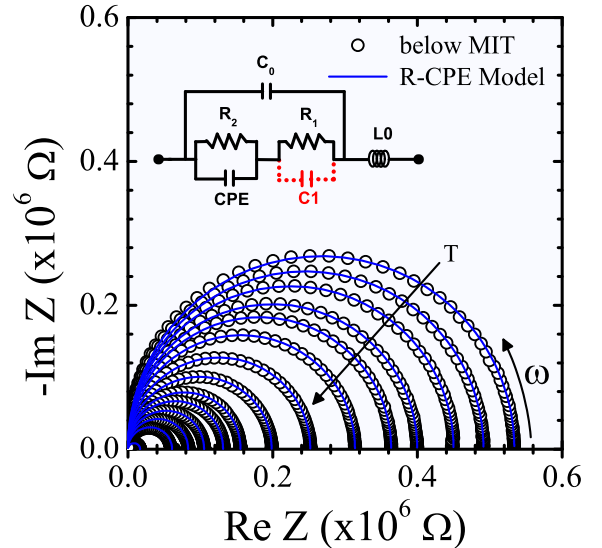


FIG. 1. (Color online) Impedance Spectroscopy measurements of a 90 nm-thick VO₂ thin film at a frequency range 100 Hz - 1 MHz from 292 K to 338K (open circle). Line (blue) corresponds to the R-CPE fit. The inset depicts the best equivalent circuit, C1 is indicated but not included in the fitting procedure

Hz to 10 MHz. The amplitude of the voltage signal was varied between 0.1 to 1 V; 0.5 V was found to be the optimal voltage in terms of a low signal-to-noise ratio without producing any significant heating to the sample. In order to avoid parasitic effects in the measurement a custom-built sample stage was used and 99.99% pure Indium was used to connect 0.1-thick 10cm-long copper wires to the sample. Our sample stage allowed varying the temperature between 290 K and 360 K. Around 500 curves were taken in order to map the temperature dependence of impedance. IS data from VO₂ thin films between room temperature and 333 K are shown in Fig. 1 but only a few selected ones are shown. Once the temperature is increased the sample resistance starts to change and the impedance response shows smaller semicircles. Our data in Fig.1 shows signs of one single, slightly "non-ideal" dielectric relaxation, manifested by one slightly depressed semicircles for each temperature, where the center of each semi-circle has shifted below the x-axis (real-Z). In case of an ideal Debye-relaxation as represented by an ideal parallel resistor-capacitor element a perfect semicircle is expected^{16,17}.

In order to investigate the capacitance trend as first approach we extracted the effective capacitance C_E directly from the impedance data (see open-circle symbols in Fig.1) where VO₂ is in the insulating regime around the transition. The capacitance is obtained from the frequency ω_x at which the semicircles are maximum. In this region we have $\tau\omega_x = 1$ where $\tau = RC_E$. In this limit R corresponds to the real part of the impedance and C_E is the equivalent capacitance plotted in Fig. 3a. C_E slightly decreases between room temperature and 330 K and more interestingly increases appreciably as it approaches the MIT. Considering that only the sample and electrode interface are subject to temperature variations, any contribution to the impedance from the experimental setup (wires plus apparatus) should be temperature independent. Therefore these observations reflect the capacitance changes in the VO₂ sample. In order to further look into this we must deconvolute the different contributions to the data i.e. sample, interface and setup. With this aim an equivalent circuit was used to fit the experimental data. We used a different equivalent circuit in the VO₂ insulating and metallic phase. The best equivalent circuit for the IS data below the MIT is depicted in the inset of Fig. 1 (R-CPE model)^{14,18}. Here C0 corresponds to the stray capacitance of our setup, and was found to be around 0.1 pF at all frequencies. Note that given this value it is very unlikely to observe the capacitance of the film at room temperature, because the in-plane configuration gives an estimated film capacitance close to 5×10^{-17} Farads¹⁹, too small to be detected by the instrument due to the stray capacitance of our setup. This value is assuming a single insulating phase material with a relative permittivity of 40. The R1-C1 element accounts for sample resistance-capacitance. C1 has been removed due to its small value compared to C0 (see circuit sketch in Fig. 1).

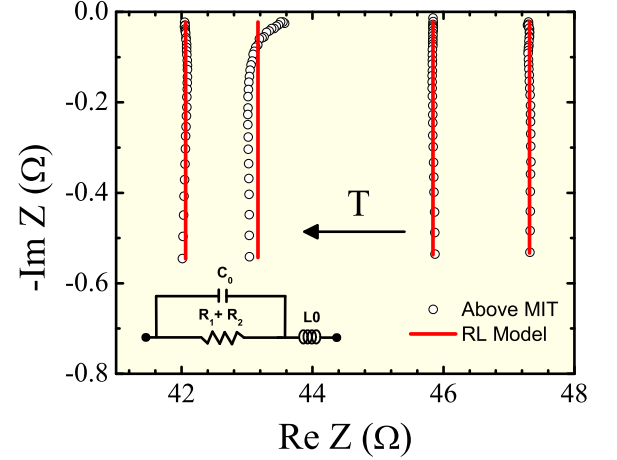


FIG. 2. (Color online) High-temperature Impedance Spectroscopy measurements of a 90 nm-thick VO₂ thin film at a frequency range 100 Hz - 1 MHz from 335 K to 343K (open circle). Line (red) corresponds to the RL model fit. Inset depicts the models elements.

The Constant Phase Element (CPE) far below the transition has an impedance of the form $Z_{CPE} = (C_m(i\omega)^n)^{-1}$ where C_m could be interpreted as Indium-VO₂ interface capacitance in modified units [Fs^{n-1}]. R2 accounts for the interface resistance and the exponent n describes the "non-ideality" of the relaxation process²⁰. Above 334 K the R2 resistance drops dramatically and the IS response is better described by an RL circuit as shown in Fig. 2. The imaginary part is now dominated by the wire inductance $L0$, around 1×10^{-4} H and the total resistance measured is a combination in series of the sample-bulk, interface and wires. The model agrees satisfactorily to the experimental data. Four different curves are presented to show the change with temperature.

The fitting parameters extracted from the R-CPE model are shown in Fig. 3b,c,d. Each point in the curves represents a fit at a specific temperature, the fitting-convergence criteria (χ^2) was kept as low as 10^{-4} for all points as shown in Fig. 1 (blue-solid line). C_m was converted to C_p in Farad units employing the relation $C_p = C_m(\omega_x)^{n-1}$, for details see Ref. 21. As can be seen from Fig. 3b, the C_p decreases monotonically between room temperature and 334 K. This decrease may be consistent with metallic domains nucleation at the interface and may be understood by considering a two dimensional interface as a network of mainly parallel capacitors. Metallic domain nucleation may then be understood as "switching-off" some of these insulating parallel capacitors and, consequently, the overall interface capacitance C_p drops. By further increasing the temperature, C_p increases appreciably. This behavior cannot be explained by interface effects and should be related to metallic domains nucleation at the bulk material. The insulating bulk may also be considered a capacitor-network

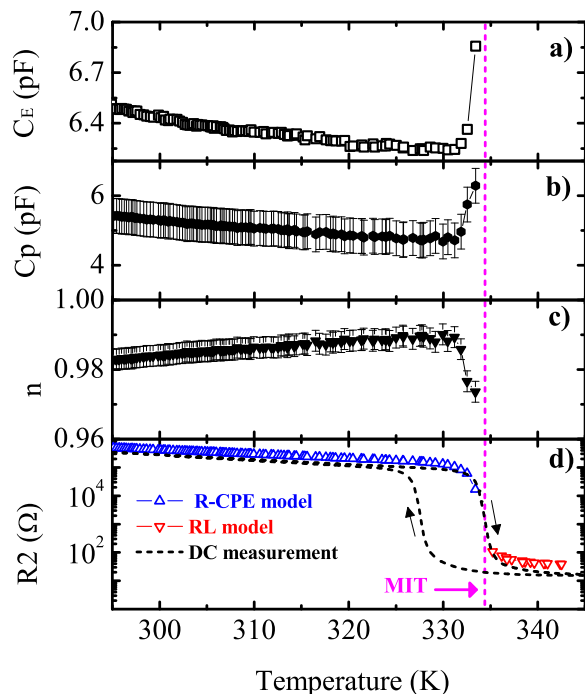


FIG. 3. Temperature dependence of a) the effective capacitance C_E , b) the CPE capacitance C_p in normal units, c) n exponent, d) the resistance R_2 , extracted from R-CPE model (up triangle symbol) below the MIT and from the RL model (down triangle symbol) after the MIT. The dashed line correspond to a DC resistance measurement. The vertical dashed line indicates the MIT.

and "switching off" some insulating capacitors leads to an increase of the overall sample capacitance, because such capacitors are now dominantly in series due to the in-plane measurement configuration. The film capacitance has been estimated though to be rather small, and, therefore, the increase in film capacitance needed to be massive (several orders of magnitude) in order to have a perceptible effect on the interface capacitance values shown (~ 6 pF) in Fig. 3a,b. Further work using out-of plane measurements may be necessary to further investigate this. From 3c it can be seen that the n exponent slightly increases with temperature below 330 K below the MIT, but a sharp decrease occurs when the temperature approaches 330 K; we believe that this is due to the high concentration of metallic domains which breaks the homogeneity across the sample. Fig. 3d shows the temperature dependence of R_2 in semilogarithmic scale. A monotonic decrease between room temperature and 334 K is followed by a sharp drop of almost two orders of magnitude within just 3 K. This is a clear manifestation of the MIT in our VO_2 films and in agreement with our previous work³. In order to confirm the R_2 data from the fit, a two-point DC measurement of resistance vs. temperature was done (dashed line Fig. 3d). A percolation path is expected to appear somewhere in the middle of

the MIT³ and once this path connects the electrodes, the resistance rapidly droops.

In conclusion, in-plane IS measurements were performed in high quality VO_2 thin films to successfully determine the dielectric response of the films at MIT. This technique allowed us to differentiate resistive and capacitive contributions to the electrical impedance of our VO_2 thin film samples and to investigate the dielectric response at the MIT near the percolation threshold. A slightly depressed semicircle behavior was found in our samples from room temperature up to 338 K. The decrease of the effective capacitance can be interpreted as an interface effect due to the metallic domains nucleation at the electrodes. Around 338 K metallic percolation across the system occurs leading to a resistance drop. Slightly below 338 K the curves of capacitance vs. temperature show an increase which could be related with formation of a network of capacitors across the electrodes. Slightly below 338 K a capacitor-network model is able to reproduce the capacitance vs temperature increase across the MIT.

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¹⁹A better estimate is not possible, because the current cross sec-

tion is not clearly defined for co-planar electrodes in in-plane measurements.

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